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DAVID W. TAYLOR NAVAL SHIP
RESEARCH AND DEVELOPMENT CENTER

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SOME UNIQUE ASPECTS OF FOULING ON COPPER
AS COMPARED TO TITANIUM OR NICKEL

by

M. E. Schrader and J.A. Cardamone

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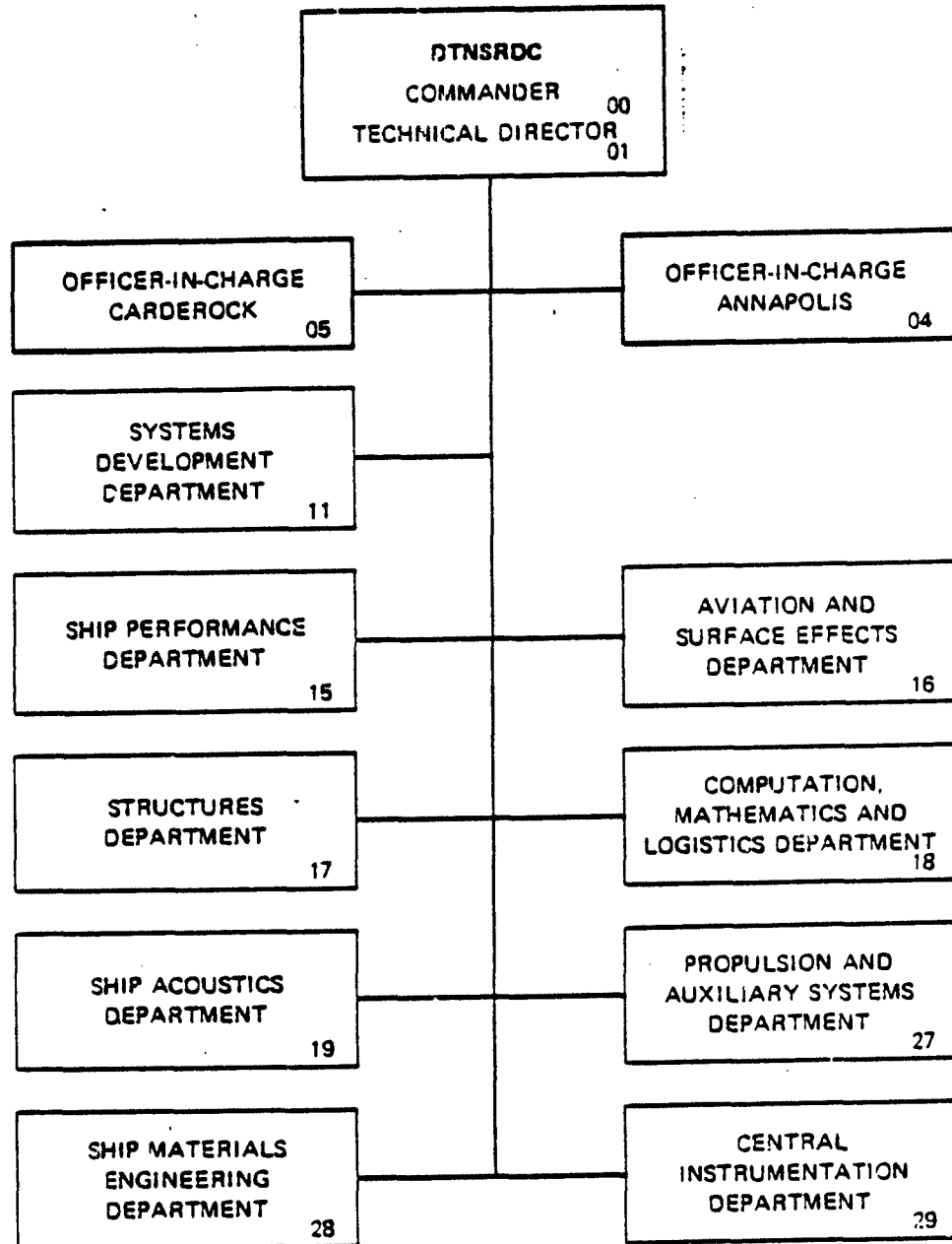
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molecular films adsorbed on titanium is consistent with that of carbohydrates. On copper the adsorption results in high concentrations of nitrogen, suggesting a chemical reaction of the copper surface with the adsorbed nitrogen-containing organic material. XPS studies revealed "chemical shifts" of the characteristic 1s electron binding energy of nitrogen on copper as compared to nitrogen on titanium, thereby providing further evidence of the chemical reaction and indicating that the nitrogen is in reduced form. Quantitative analysis by means of XPS yields an elemental analysis of the molecular layer that is consistent with an organo-metallic copper complex with coordination number of four.

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LIST OF ABBREVIATIONS

AES	Auger Electron Spectroscopy
%	Percent
XPS	X-ray Photoelectron Spectroscopy

ABSTRACT

Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) are utilized to aid in gathering information on the nature of the molecular layer that is adsorbed to artificial surfaces immersed in seawater, and its role in subsequent bacterial adhesion. We have found by means of AES that the composition of molecular films adsorbed on titanium is consistent with that of carbohydrates. On copper the adsorption results in high concentrations of nitrogen, suggesting a chemical reaction of the copper surface with the adsorbed nitrogen-containing organic material. XPS studies revealed chemical shifts of the characteristic 1s electron binding energy of nitrogen on copper as compared to nitrogen on titanium, thereby providing further evidence of the chemical reaction and indicating that the nitrogen is in reduced form. Quantitative analysis by means of XPS yields an elemental analysis of the molecular layer that is consistent with an organometallic copper complex with coordination number of four.

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INTRODUCTION

Macrofouling of ship's hulls and other objects immersed in seawater consists of the formation of a layer, often inches thick, of material. The layer, dependent primarily on the attachment of barnacles to the surface, can have a very large effect on the function of the immersed object. When present on ship's hulls, for example, maximum speeds can be reduced and the expenditure of energy increased by as much as 50%. Prior to the formation of the barnacle layer, the phenomenon of microfouling generally takes place. This involves formation of a relatively thin layer of slime mixed with bacteria. This layer has obvious importance in that it is both a precursor to the macrofouling process and a physical connecting link between the barnacle layer and the immersed surface. Even in the absence of macroscopic fouling moreover, the slime layer itself can have a deleterious effect on the function of surfaces such as windows, condensers, and interior pipe walls.

*Definitions of abbreviations are listed on page v.

It has been found that prior to the formation of the bacterial slime layer a layer of large organic molecules, known as the "conditioning layer", adsorbs to all surfaces. Whereas formation of the barnacle layer is measured in weeks or months, and the slime layer in days or weeks, a molecular layer is present within seconds after immersion, and develops in hours. Analysis of these layers in their early stages has until now consisted essentially of thickness measurements. During the last decade techniques have become available for analyzing the uppermost atomic layers of solid surfaces or of layers adsorbed to them. In this work Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) were used to determine the composition of the outer atomic layers on copper, titanium, and also nickel surfaces, before and after immersion in biologically (potential or actual) active media. In the long run, it is anticipated that an understanding of this phenomenon will lead to methods of modifying surfaces to yield beneficial fouling properties through control of the "conditioning layer".

EXPERIMENTAL

Polished titanium alloy and copper surfaces (and, in one experiment, nickel), were immersed in various types of biological media such as cultures of the bacterium *Pseudomonas Atlantica* and a marine broth containing nutrients for bacteria. Since the initial results obtained from immersion in the bacterial culture were qualitatively the same as those obtained from the marine broth, subsequent immersions were carried out largely in the broth. Analysis of the surfaces was performed by AES and XPS with the aid of argon-ion bombardment depth profiling.

RESULTS AND DISCUSSION

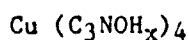
Immersion of copper, titanium, and nickel for periods of time ranging from a fraction of a minute to a fraction of an hour, resulted in stable adsorbed films which seemed similar for titanium and nickel but were clearly different for copper. The film on titanium (and nickel) consisted largely of carbon and oxygen with a small amount of nitrogen (Figure 1), consistent with the view that this layer is composed essentially of polysaccharides, or of glycoproteins. The film on copper, on the other hand, has a large nitrogen component (Figure 2) suggesting a chemical reaction of the copper surface with adsorbed nitrogen-containing organic material. An interesting feature of the results in all cases is that, after a suitable exposure period, they remain constant with time. This may be due either to cessation, or drastic slowdown, of the adsorption process, or continuation of adsorption with an adsorbate of constant composition. Since the analytical techniques see only the outermost few atomic layers, the latter phenomenon would simulate cessation of adsorption.

The anomalous results obtained with copper surfaces were especially interesting. Copper nickel alloy is a widely used naval material, and is known to possess antifouling properties with respect to macrofouling, i.e., attachment of the barnacle layer. The mechanism is generally thought to involve leaching of copper ions toxic to the barnacles. The behavior of this alloy with respect to microfouling, while not well understood or always predictable, is nevertheless clearly different than most other metallic materials. The special behavior of the copper surface to biomolecular adsorbents suggests the possibility of a direct or indirect involvement of this phenomenon in some aspects of the fouling process. The phase of this

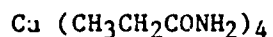
investigation reported here is essentially concerned with this copper surface phenomenon.

The employment of a sophisticated aspect of XPS known as the "chemical shift" has been found especially useful in determining the nature of the biomolecular interaction with copper surfaces. It can be seen from Figure 3 that the energy of the nitrogen peak is shifted by a small but well defined amount from its value on titanium to that on copper. The value on copper is typical of that found for reduced forms of nitrogen, such as ammonia or amino groups, thus yielding information on the chemical state of nitrogen resulting from its interaction with the surface of copper.

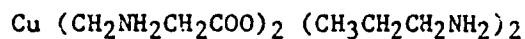
Ion bombardment of a film combined with AES can give relative values for the thickness of films by comparing the time required to remove all, or a given portion, of a film under constant bombarding conditions. The results for copper indicate continuous thickening of the film with time of immersion in marine broth. The rate of thickening however, sharply decreases with time. When the ion-bombardment is combined with XPS analysis, quantitative analysis of the film can be performed with respect to its major components, as well as an estimate of film thickness. The XPS analyses once again indicate a thickening of the film on copper with time of immersion in the marine broth. This can be seen by a lowering of the atomic percent of substrate-copper achievable for a given time of ion bombardment. The most striking information provided by the XPS quantitative analysis however, can be seen by comparing the atomic percent of copper, carbon, oxygen, and nitrogen present on the outer layer of the film at the onset of ion bombardment (Table 1). These are reasonably constant for all times of immersion. and correspond to an empirical formula



where x is unknown since H is not detectable by XPS. A number of plausible structures may be written for this formula such as, for example,



a copper propanamide. In view of the known chemistry of copper however, we suggest the following compound,



which would come about by interaction of $\text{CH}_2\text{NH}_2\text{CH}_2\text{COOH}$ (-alanine) and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (propylamine) with the copper surface. Other isomers of alanine and propylamine, of course, are also possibilities in this category.

TABLE 1 - COMPARISON OF EXPERIMENTAL AND THEORETICAL COMPOSITION
OF OUTER LAYER OF CORROSION FILM ON COPPER

Element	Atomic % From XPS Data	Atomic % of Proposed Formula
Cu	4.2	4.8
C	59.1	57.1
O	17.0	19.0
N	19.7	19.6

CONCLUSIONS

Conditioning films many molecules thick can form within minutes on artificial surfaces immersed in seawater. Auger electron spectroscopic and x-ray photoelectron spectroscopic measurements show that the film formed on copper is unique in that it results from a continuing surface reaction rather than mere adsorption. Quantitation of the XPS results indicates that at all thicknesses, the composition of the outer layer of the film is consistent with the formula for an organometallic copper complex with coordination number of four. This result is expected to play an important role in interpreting the unusual behavior of copper and copper alloys with respect to marine fouling.

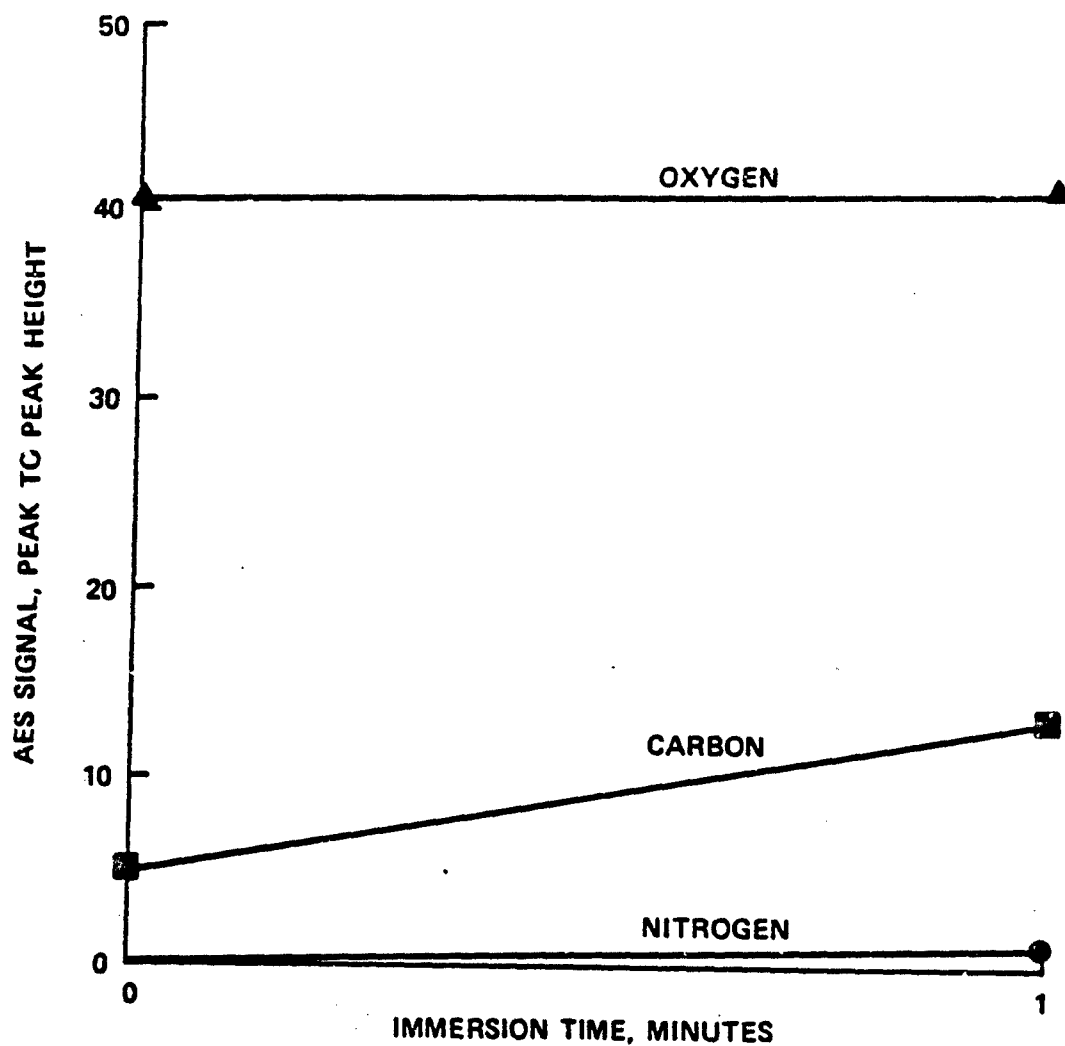


Figure 1 - AES of Polished Titanium Surface Exposed to *Pseudomonas Atlantica*

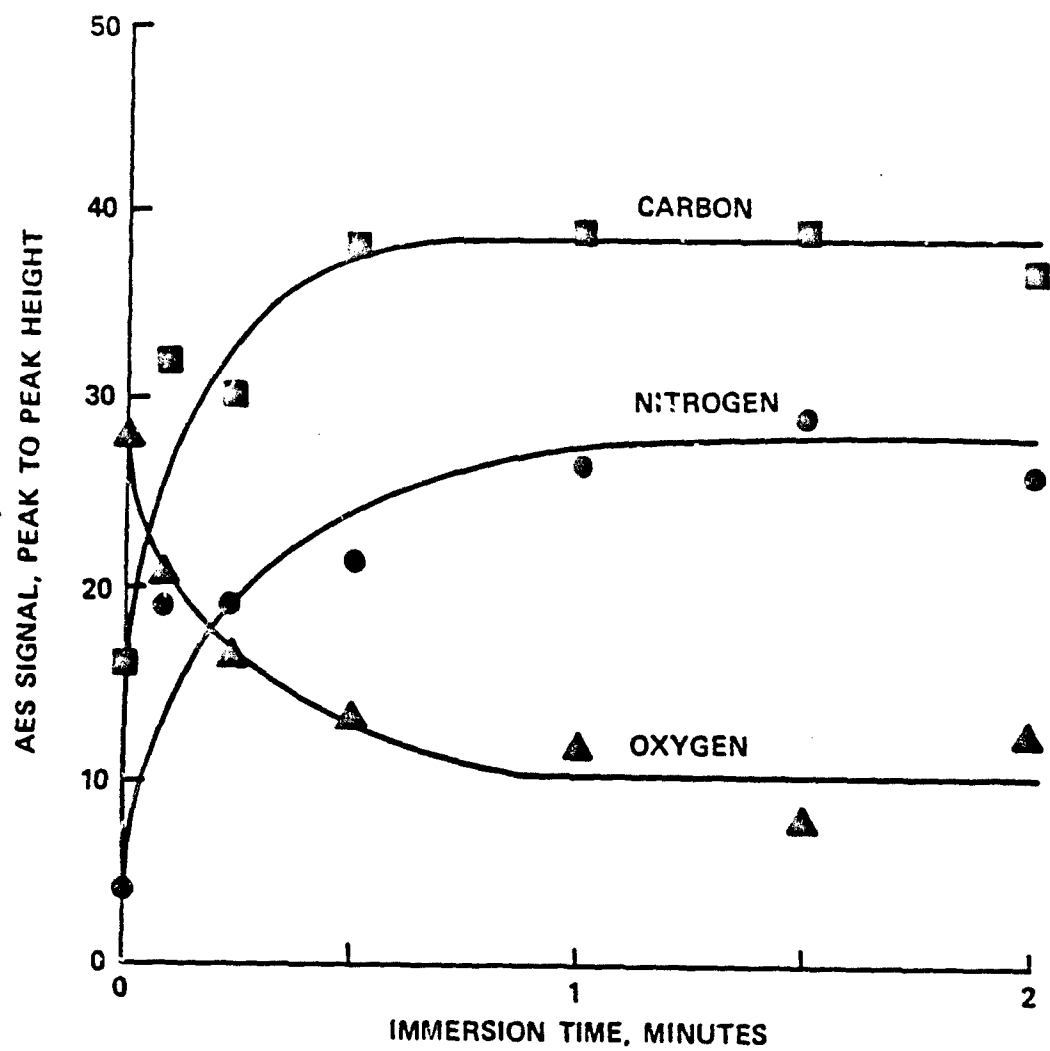


Figure 2 - AES of Polished Copper Surfaces Exposed to Pseudomonas Atlantica

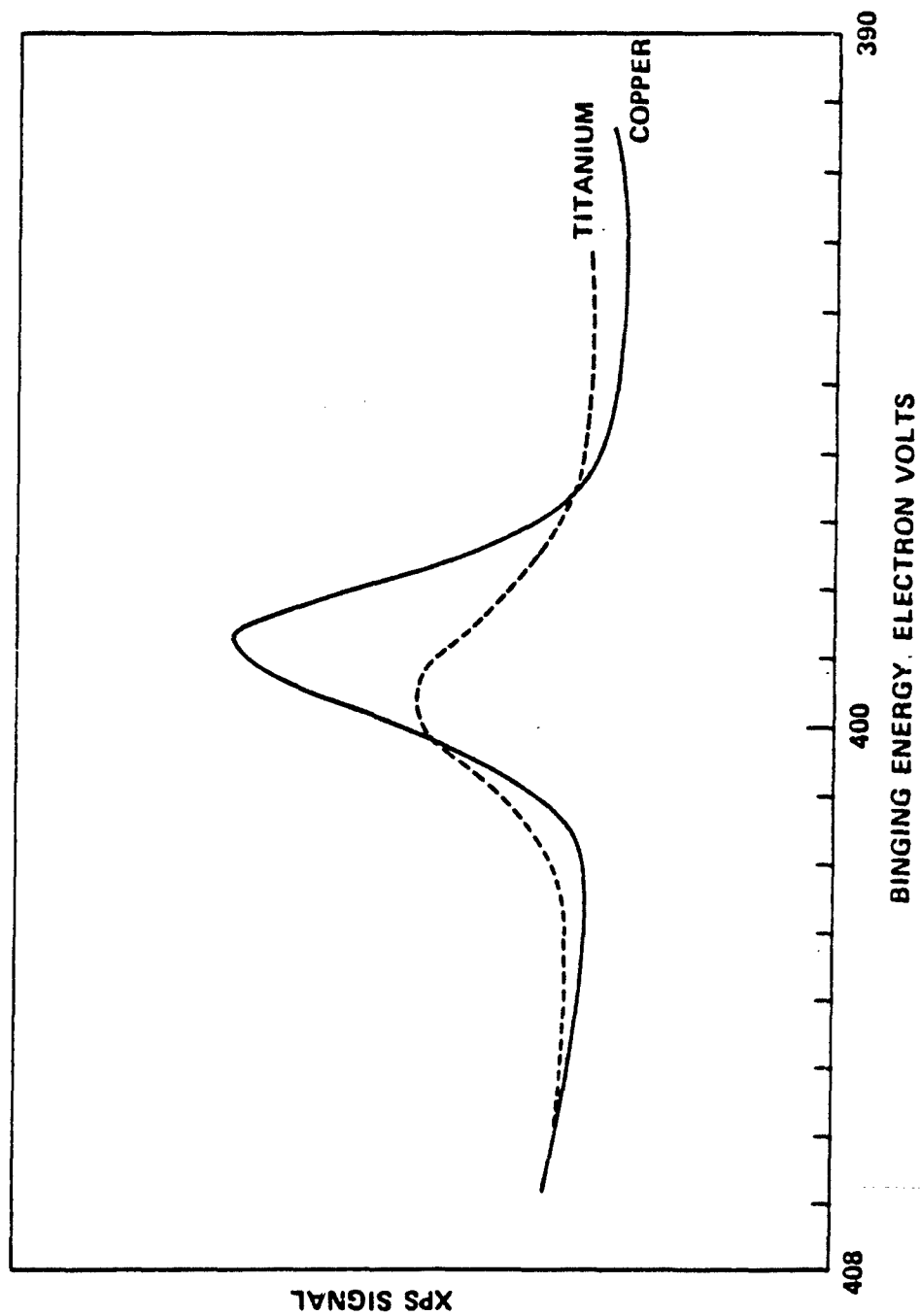


Figure 3 - Chemical Shift of XPS Nitrogen Peak: Copper and Titanium Surfaces
(30 Minute Immersion)

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